

OXIDATION STUDIES ON COKING COAL RELATED TO WEATHERING

Part II: The Distribution of Absorbed Oxygen in the Products Resulting from the Pyrolysis of Slightly Oxidized Coking Coal

by

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INTRODUCTION

In the previous paper (1) of this series, the reduction of the dilatation of coking coal caused by oxidation in air (2) was studied in connection with the development of a more sensitive and a more generally applicable method of detecting trace oxidation of coal. It was found *inter alia*, that for Moss 3⁺ coal, the decrease in dilatation was a very sensitive indicator of the degree of oxidation. The total oxygen content, measured by neutron activation, was 8.55%. A relatively insignificant increase in the oxygen content of this coal by an additional 0.2% to 0.4% caused a decrease of the dilatation from 15% to 25%. The exposure of a minus 20-mesh, fresh sample of this coal for three days in the laboratory, at room temperature caused a marked decrease (5% to 10%) in the dilatation. An increase of the oxygen content in this coal by approximately 1.3%, bringing the total to 9.85%, caused the complete disappearance of both coking and dilatation properties. This level of oxygen content was reached after air oxidation of this coal in an oven at 100°C for 72 hours.

There are some differences of opinion on the subject of the mechanism of the low-temperature oxidation of coal. However, on the basis of a number of papers (3, 4, 5, 6), the conclusions are that low-temperature oxidation from a chemical point of view leads only to:

1. An increase in the reactive oxygen groups (-OH, - COOH, C=O).
2. A small decrease in the aliphatic and alicyclic carbon and hydrogen content of coal.

+ ASTM Classification, high-volatile A bituminous coal, International Classification of Hard Coals 535.

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It was therefore of considerable interest to examine in greater detail the manner in which small changes in the reactive-oxygen groups affect certain physicochemical properties of coking coal, for instance, dilatation. It seemed to us that any light that could be shed on this problem would be of great significance from the point of view of understanding the role of oxygen in the chemistry of the coking process. This investigation was therefore aimed at clarifying certain aspects of this problem.

EXPERIMENTAL

The investigations were conducted mainly on Moss 3 coal, though Itmann coal⁺⁺ was occasionally used.

Samples of the fresh coals, which were delivered directly from the mines, were ground in an argon atmosphere to pass the 200-mesh (Tyler) screen. Each was oxidized in the two following ways:

- by using atmospheric air, and
- by using labelled oxygen (O_2^{18}).

The oxidation by atmospheric oxygen was performed either in an oven (100° for seventy-two hours), or by use of an IR lamp (250W) under the conditions described in a previous paper (1).

Oxidation by labelled oxygen was carried out, as follows:

A 10.5-g portion of Moss 3 coal was placed in a 250-ml Erlenmayer flask. A gas-tight one-way capillary stopcock was then sealed to the top of the flask. The sample was evacuated for three hours at room temperature. Then the temperature was raised to 70°C and the evacuation continued until the inside pressure dropped to 0.2 mm of Hg. At that time, 100 ml of labelled oxygen (99.85% by volume of O_2^{18}) was introduced, followed by an equal volume of argon. The capillary stopcock was closed and the flask was sealed below the stopcock to completely exclude the introduction of atmospheric oxygen. The sealed flask was subsequently placed in an oven at 100°C for seventy-two hours. The concentration of O^{18} in such oxidized coal was 0.66% by weight. The product after oxidizing the coal with O_2^{18} is referred to as oxy- O^{18} coal.

The coal samples, which were oxidized by use of atmospheric oxygen or an IR lamp, were pyrolyzed under vacuum in the manner previously described (1), except that the total time of pyrolysis was increased from ten minutes to fifteen minutes. The pyrolysis experiments were conducted by heating successive samples of coal to successively higher temperatures, at intervals of approximately 50°C, over the range of temperature 350°C to 800°C. The

⁺⁺ASTM Classification, low-volatile bituminous coal, International Classification of Hard Coals 333.

content of carbon dioxide and carbon monoxide was analyzed in the pyrolysis gas evolved up to a given temperature using a Fisher Partitioner with a double-column hexamethylphosphoramide on Chromosorb P, followed by Linde molecular sieve 13X. Helium, with a thermal conductivity detector, was used as the carrier gas at a flow rate of 40 ml/min.

Identical experiments were conducted on samples of fresh unoxidized Moss 3 coal. The results are presented in Figure 1, which shows the difference between fresh and oxidized coal with respect to the oxygen evolved, in the form of CO and CO₂ per gram of coal, as a function of the final temperature of pyrolysis. The pyrolysis of Moss 3 coal, oxidized with O₂¹⁸, was conducted in a manner that excluded oxidation by atmospheric oxygen. After oxidation, the coal samples were transferred to the vacuum-pyrolysis apparatus described previously (1), and pyrolyzed in the temperature range 450° to 950°C. The concentrations of CO¹⁶, CO₂¹⁶, CO¹⁸, CO₂¹⁶¹⁸ and CO₂¹⁸ in the pyrolysis gases were determined by a CEC 21-104 Mass Spectrometer.

The cokes obtained from the pyrolysis of oxy-O¹⁸ coal under a vacuum at temperatures from 100° to 950° were subjected once more to a pyrolysis process at a temperature of 1050°C. All oxygen-containing gaseous products of pyrolysis were then converted to carbon monoxide by use of a lampblack-nickel catalyst. The pyrolysis and conversion were conducted using the method described previously (7), with the exception that the composition of converted gas was analyzed by mass spectrometer. To obtain the necessary level of accuracy in determining the concentration of CO¹⁸ and CO¹⁶, it was necessary to analyze the content of C₂H₆ and C₂H₄ in the gas samples from the direct pyrolysis of oxy-O¹⁸ coal. The contents of ethane and ethylene were determined using a chromatograph (Aerograph 1500 equipped with a flame-ionization detector and a copper column, 0.25-inch ID by 30 feet length and one-quarter inch diameter, packed with silicone DC 200 on Chromosorb P). The flow rate of nitrogen used was 33 ml/min.

RESULTS AND DISCUSSION

Interesting information can be derived from Figure 1, concerning the influences of the two methods of oxidizing coal (IR lamp or oven at 100°C) on the differences in yield of oxygen, in the form of CO₂ and CO, in the resulting gaseous products from the pyrolysis of the oxidized coal (oxycoal). The conditions were selected so that the amount of oxygen absorbed by each coal during oxidation was the same for both methods of oxidation. At a given temperature of pyrolysis, more oxygen in the form of CO₂ and CO was evolved per gram of coal when samples were subjected to photo-oxidation under the IR lamp than if they were oxidized in the oven. For the samples photo-oxidized by IR lamp, the temperatures of pyrolysis for which $O_2 = O_2^{oxid} (CO_2 + CO) - O_2^{fresh} (CO_2 + CO)$ = a constant are relatively clear, and can be determined as 650°C for Itmann coal and 752°C for Moss coal. A similar plateau cannot be

found in the case of the oxidation of the coals in air in an oven at 100°C. It will also be observed that the amount of oxygen evolved in the form of CO₂ and CO during pyrolysis of the samples, oxidized at 100°C, was much lower than that when oxidation was conducted by use of an IR lamp. A possible explanation of this is that a considerable amount of oxygen absorbed by coal oxidized during the process of oxidation at 100°C, was later evolved in the form of water or linked with the tar during the subsequent pyrolysis of this oxycoal. The shapes of the appropriate curves in Figure 1 suggests this possibility.

The investigations to follow were limited to Moss 3 coal which was selected for the ease with which this coal oxidizes and for its fluid character. Labelled oxygen, O₂¹⁸, was used for the oxidation of this coal at 100°C, as previously described. It was assumed that the mechanism of the oxidation of Moss 3 coal at 100°C would resemble a somewhat accelerated weathering process. The advantages of this method of oxidation were that even though the coal was but slightly oxidized, similar to weathered coal, it was still possible to identify and determine, with precision, the low concentrations of products, such as, CO¹⁸, CO₂¹⁸, CO¹⁸O¹⁶ and H₂O¹⁸. The results obtained directly from pyrolysis of oxy-O¹⁸ coal are presented in Table I. These data are presented graphically in Figure 2 to show the different manner in which the gases are evolved. The amount of O¹⁸ in the form of CO₂¹⁸ and CO¹⁸O¹⁶ in gas from pyrolysis reaches the highest value at 450°C and remains on the same level during successive pyrolysis experiments at higher temperatures, right up to 950°C. The manner in which the CO₂¹⁸ and CO¹⁸O¹⁶ are evolved during pyrolysis of oxy-O¹⁸ coal seems to be strong evidence that some oxygen groups, created during oxidation of this coal, decompose completely to CO₂¹⁸ or CO¹⁸O¹⁶ below 450°C.

The continuous increase of O¹⁸ evolved in the form of CO¹⁸ may be observed in Figure 2, during the increase of the temperature of pyrolysis. The shape of the curve of evolution of O¹⁸ in the form of CO¹⁸ is similar to the analogous curve for CO¹⁶. However, even here, especially at lower temperatures of pyrolysis, the relative amount of evolved CO¹⁸ is much higher than for CO¹⁶.

The relatively high concentration of combined O¹⁸ in the gaseous products of low-temperature pyrolysis agrees with the independently measured rapid decrease of O¹⁸ in the resulting coke, as shown in Figure 3. About 60% by weight of O¹⁸ present in oxy-O¹⁸ coal is removed during pyrolysis of this coal at 400°C. Only about 14% of O¹⁶ is removed from the same coal during pyrolysis at 400°C. It will also be observed in Figure 3 that when the pyrolysis temperature reached 430°C, which is the temperature of maximum contraction of Moss 3 coal, a rapid decrease in the concentration of O¹⁸ and O¹⁶ in semi-coke occurred.

The evidence from the pyrolysis of oxy-O¹⁸ coal, presented in Figure 4, showed that the main part of O¹⁸ occurs in the pyrolysis product we may call

"tar + water". The data presented in this figure were obtained from a material balance derived from the results previously presented in Tables 1 and 2. This material balance was based on the quantity of coke and gas produced per gram of coal, the experimental concentrations of O^{18} in the coke and gas, and the measured initial amount of O^{18} in oxy- O^{18} coal before pyrolysis. The determination of O^{18} in the coke and gas requires some additional comment. For the determination of O^{18} in coke, the method described in the earlier paper (8) was applied, with the exception that the concentration of CO^{18} in converted gas was determined by mass spectrometry on the basis of the peak at m/e 30. The concentration of C_2H_6 in the converted gas, was found by gas chromatography to be less than $10^{-3}\%$ by volume. So, the interference by this constituent at m/e 30 should not be a serious matter. When the concentrations of CO^{18} and CO^{16} in gas from direct pyrolysis of oxy- O^{18} coal were determined, the concentrations of C_2H_6 were measured in the gas samples from each pyrolysis experiment by gas chromatography.

The results obtained were taken into account to find the proper concentrations of CO^{18} from mass spectrum. From the precautions taken and the level of reproducibility, it was considered that the concentrations of O^{18} found in coke and gas, as shown in Figure 4, were characterized by a relatively high level of accuracy. Therefore, the calculated concentration of O^{18} in tar + water owing to its relative magnitude, should likewise have comparable accuracy. It is necessary to stress the importance of this accuracy, due to the significance attached to the oxygen present in the tar in determining the coking properties of coal, and due to the surprisingly high concentration of O^{18} in tar + water obtained from pyrolysis at $450^\circ C$. This amounts to a concentration of O^{18} in the tar + water of about 3.8% to 4.0% by weight. In spite of the fact that the tar + water consisted only of about 10% by weight of oxy- O^{18} coal, it contained approximately 60% of all O^{18} absorbed by this coal during oxidation. On the other hand, the concentration of O^{18} in the semicoke from pyrolysis at $450^\circ C$ is relatively small, that is, 15% of the labelled oxygen existing in oxy- O^{18} coal, which is approximately 0.08% to 0.1% by weight of coke.

The observation that the highest concentration of O^{18} was found in the part of the organic matter of coal, which cracks to produce tar + water during low-temperature pyrolysis, appears to be consistent with the view that this part of the organic matter of coal can be roughly identified with the most extractable part of coal. This fraction, in the opinion of many authors, is responsible for coking properties (8,9).

Removacek (9) has found that the oxidation of coking coal can cause the change of the chemical character of its chloroform extract, which becomes similar to the chloroform extract from non-coking coals. In this paper, by quite a different route, it has been found that relatively slight oxidation of coal causes the largest changes, measured by increase of oxygen, in the part of the coking coal, which can most easily be cracked during heating to form tar.

It seems highly unlikely that the mild conditions of oxidation applied in this research could basically change the structure of the tar portion of this coal other than that a number of reactive-oxygen groups were introduced. Berkowitz (8) suggests that the oxygen in the form of COOH or OH groups cannot cause the change of coking properties of coal. Though a slight increase of these groups, during oxidation of coal, can probably not bring about - by itself - so marked a change in the physico-chemical properties of coal; nevertheless, there appears to be a strong possibility that the thermal decomposition of the OH groups, created during oxidation, results in the formation of ether-type crosslinks of very considerable thermal stability. A very small number of such bonds can stiffen the whole structure, and decrease the plastic properties of coal, especially the dilatation. The tar fraction is of special significance as a potential source of ether bonds, because of the high content of oxygen shown to be introduced into this fraction. Creation of crosslink ether bonds should be accompanied by the evolution of water, in our case, H_2O^{18} . It was found by mass spectrometry that the ratio H_2O^{18}/H_2O^{16} possessed the highest value when the pyrolysis experiments were conducted at the lowest temperatures, Table 3. Mass spectrometry also revealed that approximately 0.5 ml of H_2O^{18} (in gaseous state; 760 mm of Hg; 20°C) was evolved during pyrolysis of oxy- O^{18} coal. Since there exists the same probability of evolution of H_2O^{18} as H_2O^{16} as the result of the condensation of such groups as $R_1 - O^{16}H$ and $HO^{18} - R_2$, this means that the volume of gaseous water at 760 mm of Hg and 20°C evolved from condensation reactions leading to the disappearance of dilatation properties will be approximately one ml. It can be concluded from this observation that only about 12% of the total labelled oxygen absorbed during oxidation is responsible for the loss of dilatation resulting from the ether bonds. It should be mentioned that the proportionate increase of non-reactive oxygen groups (ether groups) in cokes, that occurs on low-temperature pyrolysis has been noted by other scientists (10,11). This seems to be substantial, though not sufficient confirmation of our hypothesis that it is not the OH groups per se that cause the loss of swelling properties but the fact that these groups undergo condensation reactions as the temperature is elevated to yield ether type cross links. The search for additional support for this hypothesis will be the purpose of the next paper of this series.

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Table 1. Per cent by volume of CO₁₆, CO₁₈, CO₂¹⁶, CO₂¹⁶O₁₈, and CO₂¹⁸ in gas from the direct pyrolysis, at different temperatures, of Moss 3 coal oxygenated with O₂¹⁸.

Temperature of Pyrolysis (°C)	% By Volume				Total Gas ml/g
	CO ₁₆	CO ₁₈	CO ₂ ¹⁶	CO ₂ ¹⁶ O ₁₈	
450	4.7	1.71	5.6	3.45	23.2
500	3.9	1.04	4.1	1.62	49.2
550	5.4	0.92	3.0	1.08	74.0
600	5.1	0.73	2.4	0.76	105.0
650	5.0	0.64	2.1	0.61	132.0
700	6.5	0.51	1.8	0.48	168.0
750	6.4	0.47	1.6	0.40	201.0
800	6.9	0.52	1.4	0.35	229.0
850	7.2	0.44	1.2	0.29	280.0
900	9.1	0.55	1.1	0.24	329.0
950	9.4	0.50	1.1	0.23	354.0

Table 2. The composition of gas from pyrolysis and conversion process (1050°C) of cokes obtained from Moss 3 coal oxygenated with O₂¹⁸ and pyrolyzed at indicated temperatures.

Temperature of Pyrolysis (°C)	% By Volume						Total Gas ml/g
	CO ¹⁶	CO ¹⁸	CO ₂ ¹⁶	H ₂	CH ₄	H ₂ S	
70	17.4	1.16	0.01	81.0	0.14	0.00	712.0
350	17.3	0.68	0.03	81.4	0.19	0.00	661.6
400	16.5	0.51	0.10	82.7	0.15	0.00	640.7
450	14.5	0.27	0.00	84.9	0.15	0.21	478.2
500	15.1	0.18	0.00	84.5	0.15	0.02	413.1
550	15.9	0.13	0.12	82.6	1.10	0.10	382.1
600	17.7	0.11	0.10	81.3	0.50	0.25	332.9
650	18.2	0.11	0.12	81.3	0.14	0.10	283.1
700	19.7	0.08	0.00	81.3	0.11	0.11	224.7
750	24.1	0.08	0.10	75.1	0.05	0.11	171.7
800	21.5	0.05	0.16	78.0	0.00	0.09	137.8
850	25.3	0.07	0.10	74.5	0.00	0.07	104.4
900	27.4	0.06	0.09	71.8	0.00	0.00	70.9
950	31.4	0.04	0.01	68.2	0.03	0.00	46.5

Table 3. The percentage of H_2O^{18} in totally evolved water.

Temperature of Pyrolysis (°C)	% By Volume H_2O^{18}
450	12.4
500	11.2
550	8.3
600	6.0
650	6.4
700	6.0
750	5.9
800	5.4
850	4.9
900	4.9
950	3.6

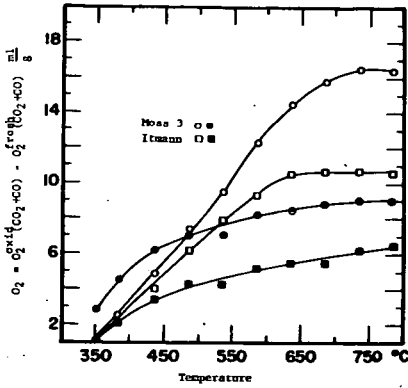


FIG. 1 The difference in the evolution of CO_2 and CO expressed as O_2 from fresh and oxidized coal as a function of the temperature of pyrolysis.

○ 15 min. IR and air
 □ 72 hr. for O_2 at 100°C

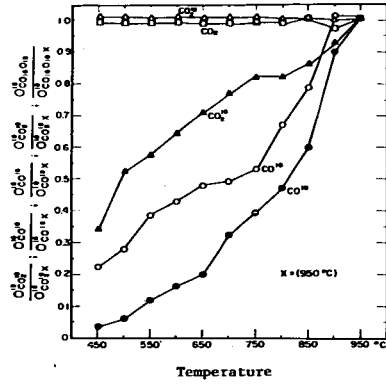


FIG. 2 The evolution of O^{18} and O^{16} in form of gaseous products of pyrolysis compared to amount of these products evolved at temperature 950°C .

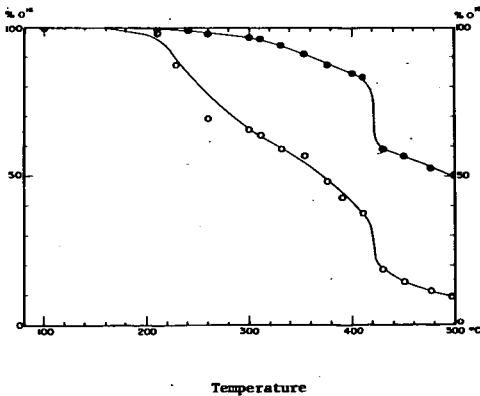


FIG. 3 Decline of the content of O^{18} and O^{16} in semicokes obtained during heating at indicated temperatures Moss 3 coal oxidized with labeled oxygen.

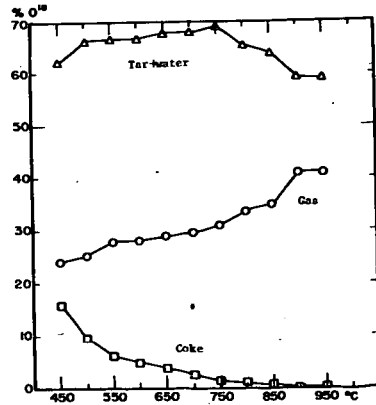


FIG. 4 Distribution of O^{18} in pyrolysis products of Moss 3 coal oxidized with labeled oxygen.